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(Invention #2)

APPLICATION FOR UNITED STATES LETTERS PATENT

for

IMPROVED OIL-BASED DRILLING FLUID

by

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This application claims the benefit of Provisional Application No. 60/023,043 filed August 2, 1996.

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to invert emulsion fluids utilized in the drilling, completion and work over of oil and gas wells.

Background

Many types of fluids have been used in the drilling of oil and gas wells. The selection of an oil-based drilling fluid, also known as oil-based mud, involves a careful balance of the both the good and bad characteristics of such fluids in a particular application, the type of well to be drilled and the characteristics of the oil or gas field in which the well is to be drilled. A surfactant capable of emulsifying incorporated water into the oil is an essential component of oil-based muds.

The primary benefits of selecting an oil-based drilling fluid include: superior hole stability, especially in shale formations; formation of a thinner filter cake than the filter cake achieved with a water based mud; excellent lubrication of the drilling string and downhole tools; penetration of salt beds without sloughing or enlargement of the hole as well as other benefits that should be known to one of skill in the art.

An especially beneficial property of oil-based muds is their excellent lubrication qualities. These lubrication properties permit the drilling of wells having a significant vertical deviation, as is typical of off-shore or deep water drilling operations or when a horizontal well is desired. In such highly deviated holes, torque and drag on the drill string are a significant problem because the drill pipe lies against the low side of the hole, and the risk of pipe sticking is high when water based muds are used. In contrast oil-based muds provide a thin, slick filter cake which helps to prevent pipe sticking and thus the use of the oil based mud can be justified.

Despite the many benefits of utilizing oil-based muds, they have disadvantages. In general the use of oil based drilling fluids and muds has high initial and operational costs. These costs can be significant depending on the depth of the hole to be drilled. However, often the higher costs can be justified if the oil based drilling fluid prevents the

1 caving in or hole enlargement which can greatly increase drilling time and costs. Disposal
2 of oil-coated cuttings is another primary concern, especially for off-shore or deep-water
3 drilling operations. In these latter cases, the cuttings must be either washed clean of the
4 oil with a detergent solution which also must be disposed of, or the cuttings must be
5 shipped back to shore for disposal in an environmentally safe manner. Another
6 consideration that must be taken into account is the local governmental regulations that
7 may restrict the use of oil based drilling fluids and muds for environmental reasons.

8 Oil-based muds contain some water, either formed in the formulation of the
9 drilling fluid itself, or residual water in the hole, or intentionally added water to affect the
10 properties of the drilling fluid or mud. In such water-in-oil type emulsions, also know as
11 invert emulsions, a emulsifier is utilized that will stabilize the emulsion. In general, the
12 invert emulsion may contain both water soluble and oil soluble emulsifying agents.

13 Typical examples of such emulsifiers include polyvalent metal soaps, fatty acids and fatty
14 acid soaps, and other similar suitable compounds that should be known to one of skill in
15 the art. The use of traditional emulsifiers and surfactants in invert drilling fluid systems
16 can complicate the clean up process in open hole completion operations. Fluids using
17 traditional surfactant and emulsifier materials may require the use of solvents and other
18 surfactant washes to penetrate the filter cake and reverse the wettability of the filter cake
19 particles. That is to say the washing with detergents should convert the oil-wet solids of
20 the filter cake into water-wet solids. Water-wet solids in the filter cake are necessary so
21 that the subsequent acid wash can attack the particles of the mud cake and destroy or
22 remove them prior to production. The productivity of a well is somewhat dependent on
23 effectively and efficiently removing the filter cake while minimizing the potential of
24 water blocking, plugging or otherwise damaging the natural flow channels of the
25 formation. The problems of efficient well clean-up, stimulation, and completion are a
26 significant issue in all wells, and especially in open-hole horizontal well completions.

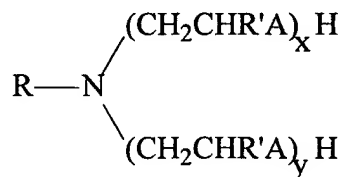
27 A typical horizontal well completion process includes one or more of the
28 following: drilling the horizontal section utilizing an oil-based drilling fluid; smoothing
29 directional corrections with a hole opener; displacing the open hole section with an
30 unused drill-in fluid to minimize solids exposed to the completion assembly; running the

1 completion assembly in to the horizontal well; displacing the drill-in fluid with a
2 completion brine; washing the filter cake with solvents and surfactants to remove or wash
3 away the oil-based drilling fluid; destroying the filter cake with an acid soak; and,
4 commencing production. Extension of the time required to clean up the open hole well
5 can result in wellbore instability and possible collapse. The collapse of a well is
6 generally considered a bad occurrence because the well will then have to be redrilled or
7 opened up if production from the formation is to occur. Thus the stability of the open-
8 hole well limits the number of steps performed before commencing production. Thus
9 there is a tradeoff between increased production due to a fully cleaned-up well bore and
10 the potential of well collapse due to instability.

11 In view of the above there exists an unmet need for an oil-based drilling fluid or
12 mud emulsion that can easily be broken in the presence of the acid soak solution. Such a
13 fluid would allow a decrease in the number of steps involved in removing the filter cake
14 and cleaning up the well which minimizes the risk of well collapse. In addition such a
15 fluid would allow for a more thorough and complete cleaning up of the well thus
16 increasing the production of the well.

18 SUMMARY OF THE INVENTION

19 Surprisingly, a novel invert emulsion fluid useful in the drilling, completing or
20 working over of a subterranean well has been invented in which the emulsion can be
21 readily and reversibly converted from a water-in-oil type emulsion to a oil-in water type
22 emulsion. In one particular embodiment, the invert emulsion fluid includes an oleaginous
23 fluid, a non-oleaginous fluid and an amine surfactant having the structure
24



1 wherein R is a C₁₂ to C₂₂ group, R' is independently selected from H, or C₁ to C₃
2 alkyl; A is NH or O and the sum of x and y is greater or equal to one but less than or
3 equal to three. The oleaginous fluid may preferably be diesel oil, mineral oil, a synthetic
4 oil and suitable combinations of these and may include at least 5% of a material selected
5 from the group including esters, ethers, acetals, dialkylcarbonates, hydrocarbons and
6 combinations thereof. The non-oleaginous fluid is preferably an aqueous liquid which
7 may be selected from the group including sea water, brine containing organic and/or
8 inorganic dissolved salts, an aqueous solution containing water-miscible organic
9 compounds, or combinations of these. In another embodiment of the present invention,
10 the invert emulsion fluid may contain a weighting agent, a bridging agent or both. Such
11 weighting agents and/or bridging agents may be selected from the group including
12 calcium carbonate, dolomite, siderite, barite, celestite, iron oxides, manganese oxides,
13 ulexite, carnalite, and sodium chloride.

14 Yet another embodiment of the present invention includes the method of
15 converting the emulsion of the present invention from an invert emulsion to a regular
16 emulsion. In this embodiment, the invert emulsion is admixed with an acid that is
17 functionally able to protonate the amine surfactant. When sufficient quantities of the acid
18 are utilized, the invert emulsion of the present invention is converted so that the
19 oleaginous fluid becomes the discontinuous phase and the non-oleaginous fluid becomes
20 the continuous phase. The conversion of the phases is reversible so that upon addition of
21 a base capable of deprotonating the protonated amine surfactant, a stable invert emulsion
22 in which the oleaginous liquid becomes the continuous phase and the non-oleaginous
23 fluid become the discontinuous phase can be formed.

24

25 DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

26 The interfacial tension between an oleaginous fluid, for example oil, and a non-
27 oleaginous fluid, for example water, is often high. Thus, if the liquids are mixed
28 together they spontaneously separate from each other when the agitation ceases, to
29 minimize the interfacial area. Lowering the interfacial tension with a emulsifier
30 enables one liquid to form a stable dispersion of fine droplets in the other. The lower

1 the interfacial tension, the smaller the droplets and the more stable the emulsion. In
2 most emulsions, the oleaginous fluid is the dispersed phase and the non-oleaginous
3 fluid is the continuous phase. However, "invert emulsions" in which the non-
4 oleaginous fluid is the dispersed phase and the oleaginous fluid is the continuous phase,
5 can be formed upon the use of a suitable emulsifier. One of skill in the art should
6 appreciate that the chemical properties of the emulsifier are important in the selection
7 of a suitable emulsifier to form a stable invert emulsion.

8 The present invention is generally directed to an invert emulsion fluid that is
9 useful in the drilling, completing and working over of subterranean wells, preferably
10 oil and gas wells. Such uses of invert emulsion fluids in such application should be
11 known to one of skill in the art as is noted in the book COMPOSITION AND
12 PROPERTIES OF DRILLING AND COMPLETION FLUIDS, 5th Edition, H.C.H.
13 Darley and George R. Gray, Gulf Publishing Company, 1988, the contents of which
14 are hereby incorporated herein by reference.

15 In one embodiment of the present invention, the invert emulsion fluid includes an
16 oleaginous fluid, an non-oleaginous fluid and an amine surfactant. The surfactant
17 component is selected so as to provide the unexpected and unobvious results substantially
18 described herein. When a majority of the amine is in its unprotonated form, an invert
19 emulsion may be formed in which the oleaginous liquid is the continuous phase and the
20 non-oleaginous liquid is the discontinuous phase. That is to say, the unprotonated form
21 of the amine surfactant is able to stabilize an invert emulsion. Upon addition of a
22 protonating agent, herein referred to as an acid, that is capable of protonating a major
23 portion of the amine surfactant, the oleaginous liquid becomes the discontinuous phase
24 and the non-oleaginous liquid become the continuous phase. In other words, the invert
25 emulsion is converted to a regular emulsion upon the addition of acid and the protonation
26 of the amine surfactant. Further, upon addition of a deprotonating agent, herein referred
27 to as a base, that is capable of deprotonating a major portion of the protonated amine
28 surfactant, an invert emulsion may be again formed; that is, the invert emulsion of the
29 present invention is reversible to an oil-in-water emulsion, and back.

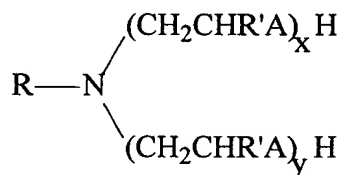
The oleaginous fluid of the present invention is a liquid and more preferably is a natural or synthetic oil and more preferably the oleaginous fluid is selected from the group including diesel oil; mineral oil; a synthetic oil, such as polyolefins, polydiorganosiloxanes, siloxanes or organosiloxanes; and mixtures thereof. The concentration of the oleaginous fluid should be sufficient so that an invert emulsion forms and may be less than about 99% by volume of the invert emulsion. In one embodiment the amount of oleaginous fluid is from about 30% to about 95% by volume and more preferably about 40% to about 90% by volume of the invert emulsion fluid. The oleaginous fluid in one embodiment may include at least 5% by volume of a material selected from the group including esters, ethers, acetals, dialkylcarbonates, hydrocarbons, and combinations thereof.

The non-oleaginous fluid used in the formulation of the invert emulsion fluid of the present invention is a liquid and preferably is an aqueous liquid. More preferably, the non-oleaginous liquid may be selected from the group including sea water, a brine containing organic and/or inorganic dissolved salts, liquids containing water-miscible organic compounds and combinations thereof. The amount of the non-oleaginous fluid is typically less than the theoretical limit needed for forming an invert emulsion. Thus in one embodiment the amount of non-oleaginous fluid is less than about 70% by volume and preferably from about 1% to about 70% by volume. In another embodiment, the non-oleaginous fluid is preferably from about 5% to about 60% by volume of the invert emulsion fluid.

The selection of a suitable amine surfactant useful in the present invention is accomplished by combining an amount of the unprotonated amine with portions of the oleaginous fluid and non-oleaginous fluid in a suitable container. The fluid is then vigorously agitated or sheared so as to intimately mix the two fluids. Upon stopping of the mixing, visual observation will determine if an emulsion has formed. An emulsion is considered stable if the oleaginous and the non-oleaginous fluids do not substantially separate after agitation. That is to say the emulsion will last for more than about 1 minute after the halting of the agitating or shearing motion that formed the emulsion. One test of whether or not an invert emulsion has formed is to take a small portion of the

emulsion and place it in a container of the oleaginous fluid. If an invert emulsion is formed, the drop of emulsion will disperse in the oleaginous fluid. An alternative test is to measure the electrical stability of the resulting emulsion using an commonly available emulsion stability tester. Generally in such tests, the voltage applied across two electrodes is increased until the emulsion breaks and a surge of current flows between the two electrodes. The voltage required to break the emulsion is regarded in the art as a measure of the stability of the emulsion. Such tests of emulsion stability should be well known to one of skill in the art as is evidenced by described on page 166 of the book COMPOSITION AND PROPERTIES OF DRILLING AND COMPLETION FLUIDS, 5th Edition, H.C.H. Darley and George R. Gray, Gulf Publishing Company, 1988, the contents of which are hereby incorporated herein by reference.

In view of the above selection criteria, in one embodiment of the present invention the amine surfactant should have the general formula



wherein R is C₁₂-C₂₂; R' is independently selected from hydrogen or C₁ to C₃ alkyl group; A is NH or O, and x+y has a value greater than or equal to one but also less than or equal to three. Preferably the R group may be a C₁₂-C₂₂ aliphatic hydrocarbon and more preferably is a non-cyclic aliphatic. In one embodiment the R group contains at least one degree of unsaturation that is to say at least one carbon-carbon double bond. In another embodiment the R group may be a commercially recognized mixture of aliphatic hydrocarbons such as soya, which is a mixture of C₁₄ to C₂₀ hydrocarbons, or tallow which is a mixture of C₁₆ to C₂₀ aliphatic hydrocarbons, or tall oil which is a mixture of C₁₄ to C₁₈ aliphatic hydrocarbons. In another embodiment, one in which the A group is NH, the value of x+y is preferably two with x having a preferred value of one. In yet another embodiment in which the A group is O, the preferred value of x+y is two with the

1 value of x being preferably one. Preferred examples of commercially available amine
2 surfactants include Ethomeen T/12 a diethoxylated tallow amine; Ethomeen S/12 a
3 diethoxylated soya amine; Duomeen O a N-oleyl-1,3-diaminopropane, Duomeen T a N-
4 tallow-1,3-diaminopropane, all of which are available from Akzo.

5 The amount of amine surfactant present in the invert emulsion fluid of the present
6 invention, as noted above, should be sufficient to stabilize the invert emulsion according
7 to the above noted test. That is to say the emulsion will last for more than about 1
8 minute after the halting of the agitation or shearing motion that forms the emulsion.
9 While the concentration may vary depending on the particular components in the
10 drilling fluid or mud, typically the concentration is less than about 10 % by volume of
11 the fluid. Thus in one embodiment the amine surfactant is preferably present in the
12 invert emulsion fluid at a concentration of 0.1% to 5.0%. More preferably the amount of
13 amine surfactant present should be present in a concentration of 1 to 5% by volume of the
14 fluid.

15 As previously noted above, it has been unexpectedly found that the addition of a
16 protonating agent causes the conversion of the invert emulsion, that is to say a water-in-
17 oil type emulsion, into a regular or conventional emulsion, that is to say an oil-in-water
18 type emulsion. The protonating agent, herein referred to as an "acid", must be
19 functionally capable of protonating the amine surfactant. Further, the acid should be of
20 sufficient strength to protonate the amine surfactant so as to cause the conversion of the
21 emulsion from an invert emulsion to a regular emulsion. In one embodiment this amount
22 is greater than about 1 equivalent of acid and preferably is about 0.1 to about 5
23 equivalents. Compounds that are suitable for use as an acid include, mineral acids and
24 organic acids preferably soluble in water. Preferred mineral acids include hydrochloric
25 acid, sulfuric acid, nitric acid, phosphoric acid, hydrofluoric acid, hydrobromic acid and
26 the like. Preferred organic acids include citric acid, tartaric acid, acetic acid, propionic
27 acid, glycolic acid, lactic acid, halogenated acetic acids, butyric acid, organosulfonic
28 acids, organophosphoric acids, and the like. Compounds that generate acid upon
29 dissolution in water may also be used, for example, acetic anhydride, hydrolyzable esters,
30 hydrolyzable organosulfonic acid derivatives, hydrolyzable organophosphoric acid

1 derivatives, phosphorus trihalide, phosphorous oxyhalide, anhydrous metal halides, sulfur
2 dioxide, nitrogen oxides, carbon dioxide, and similar such compounds. Typically, fatty
3 acids should be avoided or used in small amounts so as to not interfere with the
4 reversibility of the amine surfactant system.

5 In yet another embodiment of the present invention, other surfactant compounds
6 may be used in conjunction with the amine surfactants utilized herein. In such cases it is
7 important however that the quantity and nature of these supplemental surfactants not
8 interfere in the ability and properties given the emulsion fluid by the amine surfactant to
9 act as described herein.

10 The fluids of the present invention are especially useful in the drilling,
11 completion and working over of subterranean oil and gas wells. In particular the fluids
12 of the present invention are useful in formulating drilling muds and completion fluids
13 that allow for the easy and quick removal of the filter cake. Such muds and fluids are
14 especially useful in the drilling of horizontal wells into hydrocarbon bearing
15 formations.

16 The method used in preparing the drilling fluids of the present invention is not
17 critical. Conventional methods can be used to prepare the drilling fluids of the present
18 invention in a manner analogous to those normally used, to prepare conventional oil-
19 based drilling fluids. In one representative procedure, a desired quantity of oleaginous
20 fluid such as a base oil and a suitable amount of amine emulsifier are mixed together and
21 the remaining components are added sequentially with continuous mixing. An invert
22 emulsion of the present invention is formed by vigorously agitating, mixing or shearing
23 the oleaginous fluid and the non-oleaginous fluid.

24 The fluids of the present invention may further contain additional chemicals
25 depending upon the end use of the invert emulsion so long as they do not interfere with
26 the reversibility of the invert emulsion fluids described herein. For example, wetting
27 agents, organophilic clays, viscosifiers, weighting agents, bridging agents and fluid loss
28 control agents may be added to the fluid compositions of this invention for additional
29 functional properties. The addition of such agents should be well known to one of skill in
30 the art of formulating drilling fluids and muds. However, it should be noted that the

addition of such agents should not adversely interfere with the properties imparted by the amine surfactant as described herein.

Wetting agents that may be suitable for use in this invention include, crude tall oil, oxidized crude tall oil, surfactants, organic phosphate esters, modified imidazolines and amidoamines, alkyl aromatic sulfates and sulfonates, and the like, and combinations or derivatives of these. However, the use of fatty acid wetting agents should be minimized so as to not adversely effect the reversibility of the invert emulsion disclosed herein. Versawet® and Versawet®NS are examples of commercially available wetting agents manufactured and distributed by M-I Drilling Fluids L.L.C. that may be used in this invention. Silwet L-77, L-7001, L7605 and L-7622 are examples of commercially available surfactants and wetting agents manufactured and distributed by Union Carbide Chemical Company Inc.

Organophilic clays, normally amine treated clays, may be useful as viscosifiers in the fluid compositions of the present invention. Other viscosifiers, such as oil soluble polymers, polyamide resins, polycarboxylic acids and soaps can also be used. The amount of viscosifier used in the composition can vary depending upon the end use of the composition. However, normally about 0.1 % to 6% by weight range are sufficient for most applications. VG-69 and VG-PLUS are organoclay materials distributed by M-I Drilling Fluids L.L.C., and Versa-HRP is a polyamide resin material manufactured and distributed by M-I Drilling Fluids L.L.C., that may be used in this invention.

Suspending agents suitable for use in this invention include organophilic clays, amine treated clays, oil soluble polymers, polyamide resins, polycarboxylic acids, and soaps. The amount of viscosifier used in the composition, if any, may vary depending upon the end use of the composition. However, normally about 0.1 % to about 6 % by weight is sufficient for most applications. VG-69 and VG-PLUS are organoclay materials distributed by M-I Drilling Fluids L.L.C., and Versa-HRP is a polyamide resin material manufactured and distributed by M-I Drilling Fluids L.L.C., that may be used in this invention.

1 Weighting agents or density materials suitable for use in this invention include
2 galena, hematite, magnetite, iron oxides, illmenite, barite, siderite, celestite, dolomite,
3 calcite, and the like. The quantity of such material added, if any, depends upon the
4 desired density of the final composition. Typically, weight material is added to result
5 in a drilling fluid density of up to about 24 pounds per gallon. The weight material is
6 preferably added up to 21 pounds per gallon and most preferably up to 19.5 pounds per
7 gallon.

8 Fluid loss control agents typically act by coating the walls of the borehole as the
9 well is being drilled. Suitable fluid loss control agents which may find utility in this
10 invention include modified lignites, asphaltic compounds, gilsonite, organophilic
11 humates prepared by reacting humic acid with amides or polyalkylene polyamines, and
12 other non-toxic fluid loss additives. Typically, fluid loss control agents are added in
13 amounts less than about 10% and preferably less than about 5% by weight of the fluid.

14 In view of the above, one of skill in the art should appreciate the usefulness of the
15 above described emulsion fluid. Thus one embodiment of the present invention is the use
16 of such invert emulsion fluids in the drilling, completion and workover of oil and gas
17 wells. Because many of properties of the invert emulsion of the present invention are
18 similar to those of conventional invert emulsions, the application of the fluids should be
19 straightforward.

20 One unexpected and unobvious aspect of drilling subterranean wells with the
21 invert emulsion of the present invention is that well clean-up and well stimulation are
22 much easier and quicker to carry out, especially when the well penetrates or comes into
23 contact with a producing formation. As described above, when a conventional invert
24 emulsion drilling fluid is used, cleaning up and stimulating the well may include washing
25 the filter cake with detergents and an acid wash to dissolve the filter cake particles. If
26 these operations are to be fully effective, a significant amount of aqueous detergent and
27 aqueous acid may penetrate the formation resulting in water blockages in the formation
28 which adversely affect production. In addition, time is of the essence when open hole
29 operations are being conducted because the hole can collapse unexpectedly. Thus, in one
30 embodiment of the present invention an invert emulsion fluid as described above is used

1 in the drilling, completion and workover of a well. When the fluid comes into contact
2 with a producing formation a filter cake is formed in a conventional manner. However,
3 instead of washing the hole with a detergent solution prior to acid washing, the use of the
4 drilling fluid of the present invention allows for the use of only an acid containing
5 washing solution. Thus, the acid in the acid washing solution, the acid being functionally
6 able to protonate the amine surfactant, is injected into the well so as to convert the
7 emulsion on the filter cake which initially is a water-in-oil type emulsion, into an oil-in-
8 water type emulsion. The acid protonates the amine and the previously oil-wet particles
9 of the filter cake thereby become water-wet allowing the acid to readily reach and
10 dissolve the acid soluble solids in the filter cake. Thus the removal of the oil based filter
11 cake is easier and the process of cleaning-up or stimulating the well is able to be done
12 more effectively and rapidly.

13 Another unexpected and advantageous benefit of the present invention is the
14 ability to effectively wash drill cuttings of the oil based drilling fluid. As noted above,
15 this is conventionally done with strong detergent solutions that do not allow for the
16 recovery and reuse of the drilling oil. In fact seemingly "oil-free" cuttings can contain up
17 to 30% oil absorbed to the particle surface of the cuttings. The present invention allows
18 for the replacement of some or all of the detergent solutions with an acid containing
19 solution as a washing fluid for the cuttings. In such an embodiment, the well would be
20 drilled using the drilling fluids and muds described herein. The resulting cuttings would
21 be separated from the fluid using conventional solids removal methods. The cuttings
22 would then be contacted at least once with an acid solution so as to invert the emulsion
23 coating the cuttings. That is to say the washing with acid causes the cuttings to convert
24 from being oil-wet to water-wet solids allowing the substantial removal of the oleaginous
25 liquid from the cuttings. Once substantially free of oleaginous liquid, the cuttings may be
26 further processed or disposed of. It is possible to recover the oleaginous fluid from the
27 acid wash. In such an embodiment the spent acid wash fluid is admixed with a base
28 solution, thus deprotonating the amine surfactant. This facilitates the recovery of the
29 amine surfactant and the oleaginous fluid which may then be reused in the drilling
30 operation. One of skill in the art should appreciate the benefits of such a system in that

1 the oleaginous fluid is substantially removed from the cuttings and the oleaginous fluid
2 can be recovered for reuse in the drilling operation.

3 Another embodiment of the present invention is a method for the recovery and
4 recycling of the oleaginous fluid in a used oil based drilling fluid. In such a method, the
5 invert emulsion fluids as described herein are used as the drilling, completing, or
6 workover fluid in a well. The used invert emulsion fluid is admixed with an acid, the
7 acid being functionally able to protonate the amine surfactant and being in sufficient
8 quantities so as to convert the invert emulsion to a regular emulsion. That is to say, the
9 addition of the acid protonates the amine surfactant and the water-in-oil type emulsion
10 utilized in drilling the well is converted into a oil-in-water type emulsion. Solids, now
11 substantially water-wet, may now be separated from the fluid by gravity or mechanical
12 means for further processing or disposal. The fluid may then be mixed with a base, the
13 base being functionally able to deprotonate the protonated amine surfactant. The base
14 should be in sufficient quantities so as to convert the oil-in-water type emulsion formed
15 upon the addition of acid, back to a water-in-oil emulsion. The resulting water-in-oil
16 emulsion may then be used as it is or reformulated into a drilling fluid suitable for the
17 drilling conditions in another well.

18 The following examples are included to demonstrate preferred embodiments of
19 the invention. It should be appreciated by those of skill in the art that the techniques and
20 compositions disclosed in the examples which follow represent techniques discovered by
21 the inventors to function well in the practice of the invention, and thus can be considered
22 to constitute preferred modes for its practice. However, those of skill in the art should, in
23 light of the present disclosure, appreciate that many changes can be made in the specific
24 embodiments which are disclosed and still obtain a like or similar result without
25 departing from the spirit and scope of the invention.

26 General Information Relevant to the Examples

27 These tests were conducted in accordance with the procedures in API Bulletin RP
28 13B-2, 1990. The following abbreviations are sometimes used in describing the results of
29 experimentation.

1 "PV" is plastic viscosity which is one variable used in the calculation of viscosity
2 characteristics of a drilling fluid, measured in centipoise (cp) units.

3 "YP" is yield point which is another variable used in the calculation of viscosity
4 characteristics of drilling fluids, measured in pounds per 100 square feet (lb/100 ft²).

5 "AV" is apparent viscosity which is another variable used in the calculation of
6 viscosity characteristic of drilling fluid, measured in centipoise (cp) units.

7 "GELS" is a measure of the suspending characteristics, or the thixotropic
8 properties of a drilling fluid, measured in pounds per 100 square feet (lb/100 ft²).

9 "API F.L." is the term used for API filtrate loss in milliliters (ml).

10 "HTHP" is the term used for high temperature high pressure fluid loss, measured
11 in milliliters (ml) according to API bulletin RP 13 B-2, 1990.

12 13 Example-1

14 Invert-drilling fluids are prepared according to the following formulations with an
15 oleaginous fluid to non-oleaginous fluid-ratio of 70/30. All the materials are in grams.

16 17 Formulations

Material	Mud 1	Mud 2	Mud 3
I.O. C ₁₆ -C ₁₈	125.2	125.2	125.2
Lime	2.0	2.0	2.0
VG-PLUS	2.0	2.0	2.0
NOVAMUL	10.0	-	-
Emphos PS-2227	-	5.0	-
Ethomeen T/12	-	-	10.0
25% CaCl ₂ Brine	90	90	90
CaCO ₃	293	293	293

18
19 In the above table, I.O. C₁₆-C₁₈ is an isomerized olefin available from Amoco;
20 VG-PLUS is an organophilic clay available from MI Drilling Fluids; NOVAMUL is a
21 amidoamine surfactant available from M. I. Drilling Fluids; Emphos PS 2227 is a
22 phosphate ester surfactant available from Witco Chemicals; Ethomeen T/12 is a

1 ethoxylated tallow amine available from Akzo Chemicals; and all other components are
2 technical grade chemicals commonly available.

3 The following general procedure was used in mixing the mud formulations: First
4 the oil (IO-C₁₆-C₁₈), lime and organophilic clay were mixed for 15 min. on a Hamilton
5 Beach Mixer in a suitable mixing jar. Emulsifier was added and the combination was
6 further mixed for 10 min. The calcium-chloride brine was then added and mixed for 15
7 min. The weight material (CaCO₃) was added and then jar contents were mixed for 20
8 min. The initial and heat aged fluid properties were measured at the indicated
9 temperatures.

10 The following rheologies were measured at room temperature after the above
11 formulated fluids were heat aged at 150° F for 16 hours:

12

	Mud 1	Mud 2	Mud 3
Plastic Viscosity (PV)	44	36	41
Yield Point (YP)	13	4	28
Gel Strength			
10 sec.	6	3	8
10 min.	8	5	12
Electrical Stability (E.S.)	516	303	244

13

14 The above fluids were further heat aged at 250° F for 16 hours. Upon cooling, the fluids
15 were mixed for 15 min. and the following rheological properties were measured at room
16 temperature:

17

	Mud-1	Mud-2	Mud-3
Plastic Viscosity (PV)	49	45	51
Yield Point (YP)	32	4	39
Gels			
10 sec.	15	2	16
10 min.	15	3	21
Electrical Stability (E.S.)	552	205	322

18

1 Upon review of the above results, one of skill in the art should understand that
2 stable drilling fluid formulations can be prepared utilizing amine emulsifiers of the
3 present invention.

4 Each mud formulation was treated with 10.0 ml of 17.5% hydrochloric acid
5 solution and stirred for an additional 10 min. Mud 1 and mud 2 remained invert oil-base
6 muds as indicated by measured electrical stabilities of 453 and 359 respectively.
7 However, mud 3 formulated in accordance with this invention, was converted so that the
8 non-oleaginous fluid, in this case brine, became the continuous phase and the oleaginous
9 fluid became the internal phase. As a result the mud became thick. The water-continuous
10 phase was indicated by a measured electrical stability of seven and the fluid was
11 dispersible in water.

12 One of ordinary skill in the art should understand and appreciate that the above
13 results indicate that conventional emulsifiers can not be readily converted to water-base
14 mud upon the addition of acid. However, the amine emulsifier of this invention upon
15 protonation, can result in the conversion of a water-in-oil type emulsion to an oil-in-water
16 type emulsion.

17 The hydrochloric acid treated mud 3 was then treated with 5.0g lime ($\text{Ca}(\text{OH})_2$)
18 and stirred for 15 min. The following rheological properties were obtained after
19 treatment with lime.

20	PV.	53
21	YP.	7
22	Gels	
23	10 Sec.	2
24	10 Min.	3
25	E.S.	609

26 In view of the above results, one of skill in the art should realize that upon
27 deprotonation of amine-surfactant of this invention the fluid can be converted back from
28 oil-in-water type emulsion to water-in-oil type emulsion.

Example-2

The following invert-drilling fluids were prepared according to the following formulations with an oleaginous fluid to non-oleaginous fluid ratio of 50/50.

Formulations

Material	Mud 4	Mud 5	Mud 6	Mud 7	Mud 8
IO-C ₁₆ -C ₁₈	121	121	121	121	121
Lime	1.0	1.0	1.0	1.0	1.0
VG-PLUS	2.0	2.0	2.0	2.0	2.0
Surfactant	Ethomeen T/12	Ethomeen S/12	Duomeen O	Duomeen T	NOVAMUL
(grams)	(12.0)	(12.0)	(12.0)	(12.0)	(12.0)
25% CaCl ₂	200	200	200	200	200
Brine					
Calcium	61	61	61	-	-
Carbonate					
Barite	-	-	-	66	66

In the above table the terms and abbreviations are the same as in Example 1. In addition the terms Ethomeen S/12 is an ethoxylated soya amine available from Akzo Duomeen O is a N-oleyl-1,3-diaminopropane available from Akzo Chemical; Duomeen T is a N-tallow-1,3-diaminopropane available from Akzo; and all other components are technical grade chemicals commonly available.

The above mud formulation were mixed according to the general procedure described previously in Example 1. The following initial properties were measured at room temperature.

	Mud 4	Mud 5	Mud 6	Mud 7	Mud 8
P.V.	43	42	32	35	42
YP.	12	19	4	9	21
Gels					
10 Sec.	5	6	2	5	8
10 Min.	7	8	3	6	10
E.S.	880	496	727	452	150

The above muds were heat aged at 150°F for 16 hours. The following rheological properties were then measured at room temperature.

	Mud 4	Mud 5	Mud 6	Mud 7	Mud 8
P.V.	43	44	30	36	35
YP.	13	15	9	10	15
Gels					
10 Sec.	6	6	3	5	6
10 Min.	7	7	4	7	10
E.S.	552	268	450	392	223

In view of the above data, one of skill in the art would recognize that stable invert emulsion muds can be prepared utilizing various emulsifiers including those of this invention.

The above heat aged muds 4-8 were treated with 15 ml. of 17.5% hydrochloric acid solution. After mixing for 10 min. the following data were obtained.

	Mud 4	Mud 5	Mud 6	Mud 7	Mud 8
P.V.	22	27	31	to	30
YP.	1	1	9	thick	8
Gels					
10 Sec.	2	1	9	water-wet	3
10 Min.	2	1	8	Barite	2
E.S.	5	7	6	<u>6</u>	216
Comments	Water-wet	Water-wet	Water-wet	Water-wet	Oil-wet

In view of the above data, one of skill in the art would realize the following: mud formulations 4-7 with amine surfactant of the present invention converted to oil-in-water type emulsions when treated with acid; mud formulation 8, which is representative of a conventional drilling fluid remained a water-in-oil type emulsion. These conclusions are supported by reviewing the electrical stability data in which the single digit values of mud formulations 4-7 indicate a water continuous phase. In contrast, the electrical stability data of mud formulation 8 having a value of 216 indicates that the oil remains the continuous phase.

1 Treatment of formulations 4-7 each with 5.0 grams of lime and stirring for 10
 2 min. converted back to water-in-oil type emulsions. The following are the electrical
 3 stability and rheological data of formulations 4 - 7 after such treatment:

4

	Mud 4	Mud 5	Mud 6	Mud 7
ES.	585	523	123	352
P.V.	65	59	-	35
YP.	24	16	-	16
Gels				
10 Sec.	5	4	-	6
10 Min.	7	5	-	9

5

6 One of skill in the art, upon review of the above data should appreciate that upon
 7 protonation of amine surfactants of this invention the water-in -oil type emulsion fluids
 8 can be converted to oil-in-water type emulsions. In addition, upon deprotonation of the
 9 protonated amine surfactants the oil-in-water type emulsions can be reconverted into
 10 water-in-oil type emulsions.

11

12 Example-3

13 The following demonstrate the utility of amine emulsifiers of this invention in
 14 combination with other emulsifiers.

15

16 Formulations

Material	Mud 9	Mud 10	Mud 11	Mud 12
IO-C ₁₆ -C ₁₈	125	125	125	125
Lime	2	2	2	2
Organoclay	4	4	4	4
EthomeenT/12	10	10	8	6
Wetting Agent	Emphos PS2227	VERSAWET	NOVAMUL-3, NOVAWET-1	Monamide - 150ADY
	1.5	1.5	1.5	4
Brine 25% CaCl ₂	90	90	90	90
CaCO ₃	291	291	291	291

17

1 In the above table the terms and abbreviations are the same as in previous
2 examples. In addition, the terms VERSAWET is a oxidized crude tall oil available from
3 MI Drilling; NOVAWET is a wetting agent available from MI Drilling; Monamide-
4 150ADY is available from Mona Chemicals; and all other components are technical
5 grade chemicals commonly available.

6 Mud formulations 9-12 were prepared in a manner described above in Example 1.

7 After recording the initial electrical stability of mud formulations 9-12, the muds
8 were heat aged at 250°F/16 hours. The following results were obtained on these mud
9 formulations:

10

	Mud 9	Mud 10	Mud 11	Mud 12
Initial E.S.	396	377	368	277
Heat Aged E.S.	525	375	310	350
P.V.	66	57	55	62
Y.P.	8	15	16	9
Gels				
10 Sec.	6	7	6	7
10 Min.	6	8	7	7

11
12 To a 35 ml portion of the above mud formulations 9-12, 2.0 ml of glacial acetic
13 acid was added to protonate T/12 amine surfactant. The acetic acid treated samples were
14 thick and converted rapidly to oil-in-water type emulsions. The electrical stability values
15 for each of the acid treated samples were six or lower. One of skill in the art will
16 appreciate that such low electrical stability indicates that the water is the continuous
17 phase, that is to say a oil-in-water emulsion formed. In addition, the acid treated mud
18 formulations 9-12 were water-dispersible.

19 The remaining portion of mud formulations 9-12 were contaminated with 25 ppb
20 Rev-Dust a simulated drilled solids material, and further heat aged at 250°F/16 hours.

21 The following heat aged properties were measured on these samples:

22

	Mud 9	Mud 10	Mud 11	Mud 12
ES.	426	486	400	687
P.V.	85	88	76	84

YP.	17	20	19	6
Gels				
10 Sec.	6	8	8	7
10 Min.	7	12	11	9
High Temp	7.0	6.0	4.4	4.0
High Pressure				
Fluid Loss				
at 200°F.				

The above heat-aged and Rev-Dust contaminated samples were further contaminated with 17.5 ml of sea-water, mixed for 30 min. and heat aged at 250°F/16 hours.

The following rheological properties were measured for the resulting samples:

	Mud 9	Mud 10	Mud 11	Mud 12
ES.	980	2000+	2000+	780
P.V.	100	107	93	83
YP.	29	32	36	18
Gels				
10 Sec.	11	12	11	9
10 Min.	20	17	14	10

To the resulting muds, 50% by volume of water and 10 g of glacial acetic acid were added and the mixture stirred for 10 min. The electrical stability value for each sample was six or less. In addition the muds were dispersible in water indicating that water was continuous phase.

Given the above results, one of skill in the art should realize that invert emulsion drilling fluids can be prepared utilizing the amine surfactants of this invention in combination with other conventional surfactants. In addition, these fluids can tolerate the addition of common contaminants and can still be converted from water-in-oil type emulsions to oil-in-water type emulsions upon protonating the amine surfactants.

Example-4

The following mud formulations were prepared to demonstrate the use of different oleaginous materials using the amine surfactants of the present invention.

1

2 Formulations

Material	Mud 13	Mud 14	Mud 15	Mud 16
Oil	LVT-200	dioctyl carbonate	Diesel	Sarapar-147
(gm)	(120)	(120)	(120)	(120)
Lime	1.0	1.0	-	1.0
VG-PLUS	2.0	2.0	2.0	2.0
Ethomeen T/12	12	12	12	12
25% CaCl ₂ Brine	190	190	190	190
CaCO ₃	66	66	66	66

3

4 In the above table the terms and abbreviations are the same as in previous
 5 examples. In addition the terms, LVT-200 is a mineral oil available from CONOCO Oil
 6 Co. dioctyl carbonate is available from Huntsman Chemical; Sarapar-147 is a paraffin
 7 hydrocarbon available from Shell Oil Company (Singapore); and all other components
 8 are technical grade chemicals commonly available.

9 The above muds were made in accordance with the procedure given above in
 10 Example 1.

11 The following initial rheologies were measured at 120°F.

12

	Mud 13	Mud 14	Mud 15	Mud 16
ES.	229	512	239	313
P.V.	21	53	41	34
YP.	16	124	31	7
Gels				
10 Sec.	8	60	13	4
10 Min.	8	61	17	5

13

14 The above mud formulations were heat aged at 150°F/16 hours. The following
 15 rheologies were measured at 120°F.

16

	Mud 13	Mud 14	Mud 15	Mud 16
ES.	279	35	299	245
P.V.	27	thick	45	29
YP.	10		32	8
Gels				

10 Sec.	6	15	6
10 Min.	7	17	7

The above mud formulations were treated with 10 ml of 17.5% hydrochloric acid solutions. The electrical stability of each formulation dropped to six and became water dispersible. One of skill in the art would readily appreciate that this information indicated that the initial water-in-oil type emulsion formed was converted to an oil-in-water type emulsion upon the protonation of the amine surfactant.

Upon treating with 4.0 ml of 50% sodium hydroxide or 5.0 g of lime, the above acid treated mud formulations converted back from being oil-in-water type emulsions to water-in-oil type emulsions. The electrical stability of these alkali treated muds were as follow:

	Mud 13	Mud 15	Mud 16
E.S.	552	543	512

Upon treatment with either hydrochloric-acid, acetic acid or lactic acid, the fluids converted to oil-in-water type emulsions with electrical stability of six. Treating the acid treated emulsions with 4.0 ml of 50% sodium hydroxide, converted the oil-in-water type emulsion into a water-in-oil type emulsion with E.S. of 500, or greater.

One of skill in the art should appreciate that the above results indicate that various types of oleaginous materials can be used to formulate invert emulsion fluids of the present invention. In addition, these invert emulsions can be converted to regular emulsions and back to invert emulsions by protonating and deprotonating the amine using various water-soluble acids and base.

Example 5

To demonstrate the utility of various acids in protonating the amine-surfactant of this invention the following formulations were prepared.

Formulations

Material	Mud 17	Mud 18
Sarapar-147	120	120
Lime	1	1
VG-PLUS	2.0	2.0
Ethomeen-T/12	120.	120.
25% CaCl ₂ Brine	190	190
Emphos-PS-2227	0.8	-
VERSAWET	-	2.20
Barite	66.	66.

In the above table the terms and abbreviations are the same as in previous examples.

The above muds were made in accordance with the procedure given above in Example 1.

The above formulations were heat aged at 150°F/16 hours. The following rheologies were measured at room temperature:

	Mud 17	Mud 18
E.S.	380	470
PV	26	26
YP	12	9
Gels		
10 sec.	6	5
1- Min.	6	6

The above mud formulations were further heat aged at 250°F for 16 hours. The following is the rheologic properties at room temperature:

	Mud 17	Mud 18
E.S.	606	750
PV	33	30
YP	9	11
Gels		
10 Sec.	4	4
10 Min.	5	5

1 Mud 17 was treated with 6 g. of solid citric acid. After 1.5 hours of mixing the
2 electrical stability was measured and had a value of six. One of skill in the art should
3 readily appreciate that such a low electrical stability value indicated that the previously
4 formed water-in-oil type emulsion mud was converted to a oil-in-water type emulsion
5 mud upon the addition of the citric acid.

6 Mud 18 was treated with 6.0 g. of glycolic acid. After a thorough mixing the
7 electrical stability was measured and had a value of six. One of skill in the art should
8 readily appreciate that such a low electrical stability value indicated that the previously
9 formed water-in-oil type emulsion mud was converted to a oil-in-water type emulsion
10 mud upon the addition of the glycolic acid.

11 Upon treatment with 5.0 g. lime or 4.0 ml of 50% NaOH both the formulations
12 converted back to water-in-oil type emulsions each having an electrical stability of 608
13 and 808 respectively.

14 Example-6

15 The following formulation was prepared to demonstrate the utility of amine
16 emulsifiers of this invention in making higher mud weight formulations using barite.

17 Formulations

Material	Mud 19
IO-C ₁₆ -C ₁₈	147.6
Lime	2.0
VG-PLUS	4.0
Ethomeen-T/12	10
Emphos PS-2227	1.5
CaCl ₂ Brine 25%	106
Barite	276

19
20 In the above table the terms and abbreviations are the same as in previous
21 examples.

22 The mud formulation was prepared in a manner described above in Example 1.

23 The following rheologies were measured at room temperature before and after
24 heat aging at 150°F for 16 hours.

1

	<u>Initial</u>	<u>Heat Aged</u>
E.S.	632	525
P.V.	40	45
Y.P.	6	7
Gels		
10 Sec.	5	5
10 Min.	6	7

2

3 Upon treating the above formulations with 10 ml 17.5% hydrochloric acid the
4 electrical stability dropped to 6. The mud was too thick to measure the rheological
5 characteristics. The heat aged mud was found to be water-dispersible. One of skill in the
6 art should readily appreciate that such a low electrical stability value and the water-
7 dispersible characteristic of the heat aged mud indicate that the previously formed water-
8 in-oil type emulsion mud was converted to an oil-in-water type emulsion mud upon the
9 addition of the acid.

10 Treatment of the mud/acid mixture with 5.0 g. lime converted the oil-in-water
11 type emulsion back to a water-in-oil type emulsion as evidenced by the measurement of
12 an electrical stability of 189.

13

14 Example 7

15 The following formulations were prepared to demonstrate the utilization of fatty
16 acid ester and dialkylcarbonate as oleaginous material in preparing the mud formulations
17 of this invention.

18

19 Formulations

Material	Mud 20	Mud 21
Fina Green	188	-
Mixed dialkyl carbonate	-	188
Lime	1.0	1.0
Organophilic Clay	2.0	2.0
T/12	12.0	12.0
25% CaCl ₂ Brine	98	98
CaCO ₃	76	76

20

1
2 In the above table the terms and abbreviations are the same as in previous
3 examples. In addition the terms, Fina Green is a fatty acid ester available from Fina
4 Petroleum Corp.; Mixed dialkylcarbonate is a mixture of aliphatic dialkyl carbonates
5 available from Enichem Chemicals; and all other components are technical grade
6 chemicals commonly available.

7 The mud formulations were prepared in a manner described above in Example 1.

8 The above formulations, mud 20 and mud 21 were heat aged at 150°F for 16
9 hours. The heat aged rheologies were measured at 100° F.

	Mud 20	Mud 21
E.S.	884	645
P.V.	89	53
Y.P.	37	18
Gels		
10 Sec.	22	10
10 Min.	27	14

11
12 The above mud formulations when treated with 10 ml of 17.5% hydrochloric acid,
13 electrical stability values dropped to 18. Both mud formulation were water dispersible.
14 One of skill in the art should readily appreciate that such a low electrical stability value
15 and the water-dispersible characteristic of the heat aged mud indicate that the previously
16 formed water-in-oil type emulsion mud was converted to an oil-in-water type emulsion
17 mud upon the addition of the acid.

18 Upon treatment with 5.0 g. of lime both mud formulation became water-in-oil
19 type emulsions as evidenced by the oil dispersible character of the emulsions and
20 electrical stability values of 485. One of skill in the art should appreciate that the above
21 demonstrates that the water-in-oil emulsion character of the originally formulated invert
22 emulsion was restored by the addition of the lime which deprotonated the amine
23 surfactant.

24 While the compositions and methods of this invention have been described in
25 terms of preferred embodiments, it will be apparent to those of skill in the art that

1 variations may be applied to the process described herein without departing from the
2 concept, spirit and scope of the invention. All such similar substitutes and modifications
3 apparent to those skilled in the art are deemed to be within the spirit, scope and concept
4 of the invention as it is set out in the following claims.

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